

FATTY ACIDS AND n-ALKANES IN GREEN
RIVER OIL SHALE: CHANGES WITH DEPTH

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INTRODUCTION

Many papers have been published relating fatty acids to n-alkanes in ancient sediments. Breger (1) postulated that n-alkanes may be formed in sediments by beta-keto acid decarboxylation. Jurg and Eisma (5) demonstrated in the laboratory that a homologous series of n-alkanes can be produced by heating the C₂₂ fatty acid in the presence of bentonite. Cooper and Bray (2) suggested that odd-carbon-numbered n-alkanes and odd-carbon-numbered fatty acids may be produced from naturally occurring even-carbon-numbered fatty acids by a free-radical decarboxylation mechanism. Mair (7) and Martin and coworkers (8) have discussed the relationship between fatty acids and n-alkanes in petroleum genesis.

If fatty acids are converted to n-alkanes in sediments, a distributional relationship would likely be apparent between the two compound classes. Such a relationship would be most relevant if both the acids and the alkanes were indigenous to each sample taken from one geological formation. In this respect the Green River Formation is ideal for study of the relationship between fatty acids and n-alkanes. This formation represents 6 million years of accumulation of organic debris from a highly productive Eocene lake which existed approximately 50 million years ago. A 900-foot core representing 3 million years of the Green River Formation was sampled and the fatty acids were extracted and analyzed.

An earlier paper (6) presented a correlation between the carbon number distribution of the fatty acids and the carbon number distribution of the n-alkanes in the Mahogany zone portion of the Formation. The present paper tests the postulate that n-alkanes are formed from fatty acids by maturation processes resulting from the time differential existing between the bottom and the top of the core. The results showed that both maturation and changes in organic source material explain the differences in samples taken from several stratigraphic positions in the formation.

EXPERIMENTAL

Ten oil-shale samples were taken from the Green River Formation, nine from a 900-foot core (Equity Oil Co., Sulfur Creek No. 10), and one from the Mahogany zone. The stratigraphic positions and the oil yields of the 10 samples are presented in table 1. The samples were the same as those used by Robinson and coworkers (9) in a study of the distribution of n-alkanes at different stratigraphic positions within the formation.

The samples, ground to pass a 100 mesh screen, were treated with 10 percent hydrochloric acid to remove mineral carbonates and to convert salts of acids to free acids. Two-hundred grams of each of the acid-treated samples were refluxed with 400 ml of 7 percent borontrifluoride in methyl alcohol for 6 hours. This reaction converted free and esterified acids to methyl esters. The reaction mixture was cooled, filtered, and washed with methyl alcohol until the washing was clear. The filtrate was transferred to a separatory funnel, water was added, and the solution was extracted with successive portions of carbon tetrachloride until the solvent was colorless. The carbon tetrachloride solution of the methyl esters was dried overnight using anhydrous sodium sulfate. The fatty acid methyl esters were isolated from the carbon tetrachloride solution by urea adduction.

TABLE 1. - Stratigraphic position and pyrolytic oil yields of the oil-shale samples

| Sample Number | Stratigraphic position, feet from surface | Approximate pyrolytic oil yield, gallons per ton of shale |
|---------------|---|---|
| 0 | 830 | 60 |
| 1 | 1036-1056 | 35 |
| 2 | 1056-1081 | 34 |
| 3 | 1152-1178 | 42 |
| 4 | 1236-1241 | 48 |
| 5 | 1450-1462 | 39 |
| 6 | 1597-1628 | 35 |
| 7 | 1668-1696 | 37 |
| 8 | 1786-1825 | 28 |
| 9 | 1884-1924 | 20 |

Fatty acid methyl esters were further purified by thin layer chromatography using silica gel. The thin layer plate was developed with a mixture of n-hexane, ethyl ether, and acetic acid (90/10/1). The adsorbant zone where esters occur was scraped from the plate and extracted with a solution of 10 percent methyl alcohol in carbon tetrachloride. The solvent was removed from the methyl esters by evaporation at room temperature under a stream of nitrogen. The carbon number distribution of these isolated fatty acid methyl esters was determined by mass spectrometry using the intensity parent peak as a measure of the quantity.

Carboxyl and ester contents were determined for the 10 shale samples by analytical procedures developed by Fester and Robinson (4).

RESULTS AND DISCUSSION

The fatty acid distribution with depth (table 2), shows that the predominant acid at various stratigraphic depths within the formation is not constant. The sample number, percentage, and chain length of the predominant acid of the samples are: No. 0, 16.2, C₃₀; No. 1, 14.1, C₂₄; No. 2, 21.7, C₂₈; No. 3, 9.8, C₂₈; No. 4, 16.6, C₂₄; No. 5, 9.2, C₂₈; No. 6, 12.8, C₁₄; No. 7, 12.6, C₁₄; No. 8, 12.1, C₂₈; and No. 9, 23.9, C₂₈. The C₂₈ acid is the predominant acid in five of the samples, and is among the three most abundant acids in all the other samples except samples 1 and 4 where it is present in small amounts. The C₂₀ acid content in samples 5 through 9, despite being more abundant in nature than the C₁₉ and C₂₁ acids, is less than the C₁₉ and C₂₁ acids in these samples. The C₁₈ acid is quite low in samples 1 and 2 relative to the other eight samples. The C₃₂ acid is present in large amounts only in sample No. 0. There appears to be no consistent relationship between the acids of one sample to that of another sample. This lack of relationship may be due to differences in source material or environmental changes rather than maturation changes.

Significant differences are apparent in the relative distribution of the fatty acids and the n-alkanes from published data (3,9), shown in figures 1 and 2, where the data from four samples are plotted for comparative purposes. These particular samples were chosen because they represent three stratigraphic levels below the Mahogany zone sample approximately equi-distant from each other. If maturation of sediments causes decarboxylation of fatty acids to form n-alkanes, a relationship between the distribution of the two components would be expected. Except for sample No. 0, little similarity is evident. Since the distributions correlate poorly, either the original postulate is untrue and n-alkanes are not produced from fatty acids having one more

TABLE 2. - Carbon number distributions of fatty acids

| Carbon Number | Fatty acids, wt percent of total | | | | | | | | | |
|---------------|----------------------------------|------|------|-----|------|-----|------|------|------|------|
| | Sample number | | | | | | | | | |
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 14 | 5.1 | 7.1 | 2.8 | 6.3 | 2.3 | 8.0 | 12.8 | 12.6 | 11.4 | 6.5 |
| 15 | 3.0 | 3.4 | 2.8 | 6.3 | 2.8 | 7.2 | 2.1 | 6.3 | 8.1 | 3.7 |
| 16 | 2.7 | 7.1 | 2.4 | 5.6 | 4.0 | 5.8 | 6.4 | 7.8 | 9.4 | 5.4 |
| 17 | 2.0 | 4.0 | 1.9 | 4.9 | 2.9 | 5.1 | 5.9 | 4.3 | 2.4 | 2.0 |
| 18 | 3.4 | 2.6 | 2.1 | 4.2 | 4.2 | 5.4 | 8.0 | 7.4 | 7.4 | 6.1 |
| 19 | 2.4 | 3.4 | 1.8 | 3.5 | 3.8 | 4.0 | 4.3 | 3.6 | 2.0 | 2.0 |
| 20 | 2.7 | 8.2 | 1.9 | 2.8 | 4.5 | 2.9 | 4.2 | 2.9 | 2.0 | 1.3 |
| 21 | 2.4 | 7.1 | 2.2 | 2.8 | 5.6 | 3.6 | 4.8 | 3.6 | 2.0 | 1.7 |
| 22 | 7.4 | 8.8 | 3.6 | 4.9 | 9.7 | 5.8 | 11.6 | 8.3 | 10.7 | 13.0 |
| 23 | 4.7 | 4.7 | 4.4 | 5.6 | 12.5 | 5.8 | 3.8 | 4.7 | 3.4 | 3.3 |
| 24 | 7.1 | 14.1 | 6.2 | 4.2 | 16.6 | 3.3 | 8.0 | 6.3 | 8.7 | 12.0 |
| 25 | 3.7 | 7.6 | 5.0 | 3.5 | 8.3 | 2.5 | 3.8 | 3.4 | 2.7 | 2.6 |
| 26 | 12.1 | 11.8 | 13.3 | 8.4 | 11.8 | 6.5 | 4.9 | 5.9 | 4.7 | 5.2 |
| 27 | 2.7 | 2.6 | 8.2 | 6.3 | 3.7 | 8.0 | 2.7 | 4.9 | 3.4 | 3.7 |
| 28 | 11.1 | 4.2 | 21.7 | 9.8 | 4.0 | 9.2 | 9.8 | 8.5 | 12.1 | 23.9 |
| 29 | 2.7 | 1.3 | 5.7 | 4.2 | 1.2 | 4.3 | 1.5 | 2.9 | 2.7 | 2.4 |
| 30 | 16.2 | 1.3 | 8.6 | 7.7 | 1.1 | 5.8 | 2.5 | 3.2 | 2.7 | 2.8 |
| 31 | 1.7 | 0.4 | 2.5 | 4.2 | 0.3 | 4.0 | 0.8 | 1.6 | 2.0 | 1.3 |
| 32 | 7.1 | 0.4 | 2.9 | 4.9 | 0.5 | 3.3 | 0.9 | 1.6 | 2.0 | 1.1 |

carbon atom or other factors are more significant. One factor to consider is that the fatty acids recovered from the lower portions of the core may not be representative of the acids originally present since they may be residual acids from selective maturation.

Groups of even numbered acids vary in abundance as shown graphically in figures 1 and 2. Sample No. 0 has predominant acid peaks between C₂₆ and C₃₀, sample No. 4, between C₂₂ and C₂₆, sample No. 6, between C₂₂ and C₂₈, and sample No. 9, between C₂₂ and C₂₈. The latter two samples show the greatest overall similarity.

The carboxyl content of the shale generally decreases with depth, table 3, beginning with sample No. 0 having 23.6 mg of carboxyl per gm of organic carbon and ending with sample No. 9 having 4.8 mg of carboxyl per gm of organic carbon. This general decrease in carboxyl content with depth, and a corresponding increase in the n-alkane content, as shown by Robinson and coworkers (9), implies that the fatty acids may have been converted to n-alkanes by decarboxylation.

The ester content of the samples, table 3, did not show a trend; this is in contrast to the trend shown by the acids. Random distributions found for the ester samples reflect more accurately changes in organic source material than do the acid distributions.

Maturation changes are evident in the decreasing amount of carboxyl content with depth, the increasing amount of n-alkane content with depth, and the decreasing ratio of odd to even-carbon-numbered n-alkanes. Source material or environmental changes are evident in the variations in the amount and carbon number of the dominant fatty acids, and n-alkanes and the random distribution of ester content with depth.

TABLE 3. - Carboxyl and ester contents of the
10 shale samples

| Sample Number | Carboxyl, mg/gm carbon | Ester, mg/gm carbon ^{1/} |
|------------------|---------------------------|--------------------------------------|
| 0 | 23.6 | 36.6 |
| 1 | 18.3 | 22.2 |
| 2 | 10.1 | 33.9 |
| 3 ^{2/} | -- | -- |
| 4 | 3.8 | 26.7 |
| 5 | 6.7 | 17.9 |
| 6 | 4.0 | 37.1 |
| 7 | 4.7 | 26.0 |
| 8 | 4.9 | 42.9 |
| 9 | 4.8 | 29.0 |

^{1/} Calculated as COOH^{2/} Insufficient sample.

CONCLUSIONS

The postulate that fatty acids from the organic debris in the Green River Formation may form n-alkanes of one less carbon atom was found to be subject to question. Relatable fatty acid and n-alkane distributions were shown to be present in the younger portions of the Formation but the older portions showed little relation.

Maturation and organic source material differences may account for the observed distributions of fatty acids in sections of Green River Formation oil shale. Evidence of maturation is found in the decreasing amount of odd-carbon-numbered n-alkanes and in the decreasing amount of carboxyl content with depth. Evidence of organic source material differences is found in the inconsistent distribution of the predominant fatty acids from sample to sample.

The ester content is not related to the free-acid content, indicating different formative histories.

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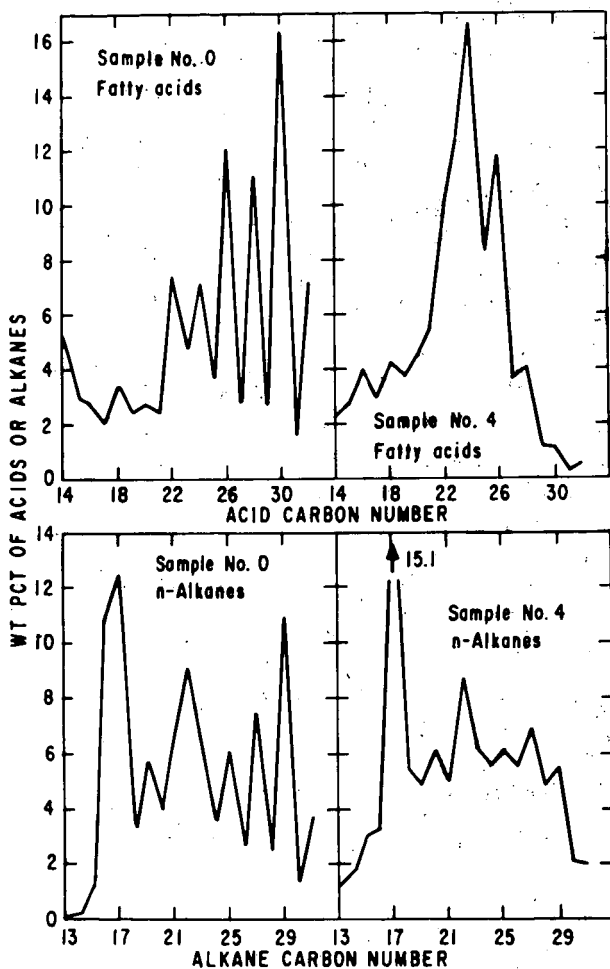


Figure 1. Comparison between fatty acid and n-alkane distributions, Sample Nos. 0 and 4

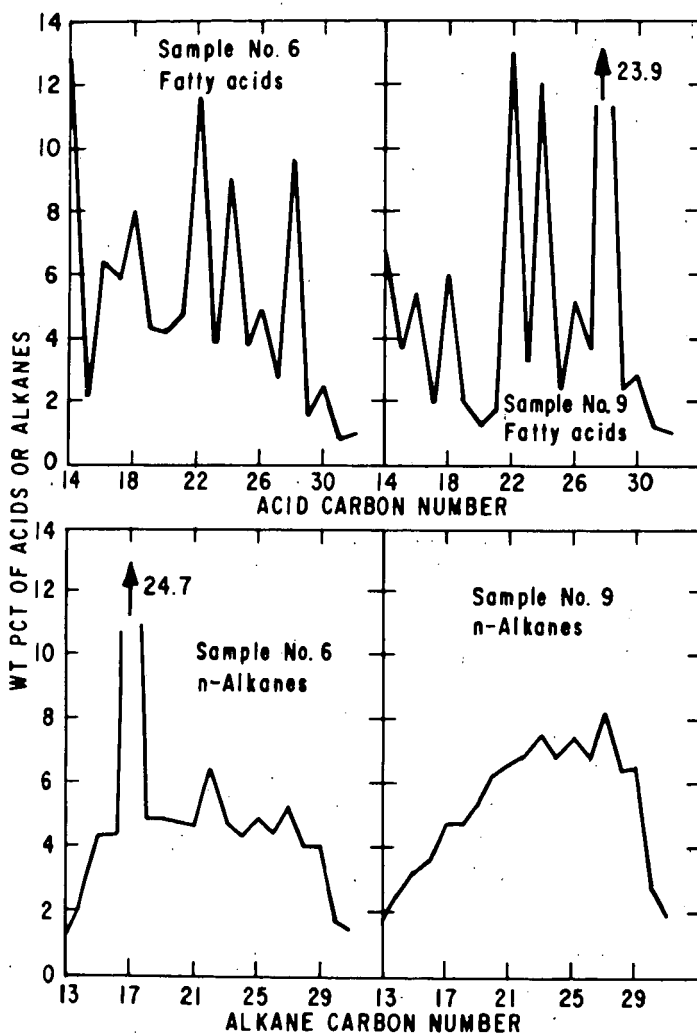


Figure 2. Comparison between fatty acid and n-alkane distributions, Sample Nos. 6 and 9